

### REMARKS

The foregoing amendments are made in light of a telephone interview conducted between Examiner Alton Pryor and the undersigned on January 5, 2007. Although no agreement was reached during the interview, the examiner did indicate he would consider various claim amendments at this time. Applicant thanks the examiner for the courtesy of a telephone interview.

Support for the foregoing amendments can be found in original claim 2 and Paragraphs [0013], [0021], [0022] and [0030] of the Specification. In particular, the working example in Paragraph [0030] shows about 35 wt.% (specifically, 37.6 wt.%) prodiamine being dissolved in N-methyl pyrrolidone. In addition, Paragraph [0021] expressly refers to the "solubility limit" as a maximum concentration, while Paragraph [0022] describes ranges with 30 wt.% and 40 wt.% as their lower limits. This is sufficient support in terms of the written description requirement for the concentration limitations added to claims 2, 6, 7 and 11. *See, In re Wertheim*, 541 F.2d 267 (CCPA 1976), cited with approval in MPEP §2163.05 III.

In his office action of September 6, 2006, the examiner states:

"If data can be provided ...that demonstrates enhanced safety (reduced flammability) in comparison with conventional granule impregnation, then the claims would be allowable."

Therefore, the following information is provided to demonstrate the enhanced safety of the inventive process in terms of reduced flammability (in particular, reduced risk of explosion) relative to conventional technology.

Conventional technology for making prodiamine-impregnated fertilizer in which powdered prodiamine is blended with particular fertilizer is inherently dangerous because powdered prodiamine is explosively flammable. *See*, Paragraphs [0003] and [0004] of the specification. In this regard, the commercial plant in which Odom Industries, Inc., a competitor of the assignee of this case, was practicing this conventional technology in Waynesburg, Miss., was destroyed by fire.

In the same time frame as this fire, a commercial supplier of prodiamine powder, Syngenta AG of Basel, Switzerland, was attempting to interest the assignee of this application, Lesco, Inc., in replacing a different herbicide Lesco was using to make herbicide-impregnated fertilizer with

powdered prodiamine purchased from Syngenta. This prompted Lesco to study the flammability of powdered prodiamine by having a number of different tests performed on that product. A copy of the conclusions drawn from that study are attached as Exhibit I. (Certain portions of this report are underscored for emphasis.)

As can be seen from this report, Barricade 65 MC (powdered prodiamine containing 65% prodiamine) combusts when dispersed in air. In addition, a powdered strip of Barricade 65 MC has a combustibility rating of 2, indicating brief ignition. Meanwhile, the maximum violence created by an exploding cloud of Barricade 65 MC has an  $St=2$ , a  $K_{st} = 265 \text{ bar} \cdot \text{meter/sec.}$ , and a maximum pressure developed on explosion of  $P_{maz} = 10.2 \text{ bar gauge}$ , thereby indicating a high maximum explosive pressure. Finally and most significantly, Barricade 65 MC is not only explosively flammable, but in addition can be electrically charged as a result of flowing through ungrounded conduits.

Additional information about the inherent dangers of explosion from handling combustible dusts can be found in attached Exhibit 2, which is a reprint from an article appearing in *Chemical Engineering Progress*.

In addition to studying the explosion dangers of Barricade 65 MC itself, Lesco invited representatives of Syngenta to visit its commercial plant in Sebring, Florida. Attached as Exhibit 3 is a copy of a trip report summarizing this meeting. Note that this trip report was prepared by Syngenta, the supplier trying to sell Lesco powdered prodiamine, not by Lesco itself. Important remarks made in this report are

“Barricade<sup>TM</sup> 65 MC has...a possible risk of explosion due to its low minimum ignition energy (MIE) at conditions most favorable to combustion.” (page 1)

\* \* \* \* \*

“Present practice is to remove dust captured by the filter bags once a day.... The concern is a dust cloud is created at the time of bag cleaning of possibly a sufficiently high concentration to require only a small amount of ignition energy to explode. The jostling of the bag assemblies from cleaning may be sufficient to move the metal parts close enough so they are able to electrically discharge through a spark to a grounded part of the dust collector.

“The hazard is a matter of probability. If enough of the powder in the dust collector is Barricade<sup>TM</sup> 65 MC or blend of other combustible dusts and the dust cloud is of

sufficient concentration at the location where a spark is generated, then there could be a dust explosion.” (page 3)

\* \* \* \* \*

“The potential hazard comes from the worker manually emptying bags. When the worker wears shoes with high electrical resistance soles, he is isolated from earth ground. There is the possibility of a static charging mechanism when powder slides by the bag surface and powder slides by powder. Charges on the bag can charge the worker. If the worker touches a grounded part of the unloading station when a sufficient dense cloud of Barricade™ 65 MC is present, there could be ignition.” (page 4)

This report clearly, eloquently and unequivocally highlights the dangers of handling powdered prodiamine in a commercial factory environment. The fact that Odom Industries’ commercial plant was destroyed by fire highlights and confirms these dangers.

In accordance with this invention, these dangers are avoided by **dissolving** the prodiamine in N-methyl pyrrolidone and using the liquid impregnant so formed for combining with the fertilizer substrate. As a result, the **fuel** responsible for the explosion risk in conventional technology (i.e. the prodiamine dust cloud) is eliminated. In addition, because prodiamine in solution does not generate static electricity when flowing through conduits, the **ignition source** responsible for igniting this fuel (i.e. static electricity generated by flowing prodiamine powder) is also eliminated. For this reason, and because N-methyl pyrrolidone has a relatively low vapor pressure, the risk of explosion inherent in the conventional technology is essentially eliminated.

Moreover, because prodiamine dissolves in N-methyl pyrrolidone in relatively high concentration, and because N-methyl pyrrolidone is non-toxic and environmentally-friendly, **uniform** application of a relatively **high concentration** of prodiamine (e.g., 0.1 to 2 wt.%) P can be easily achieved using only a minimum amount of an essentially benign carrier.

Applicant is not claiming to be the first to combine prodiamine with fertilizers. Nor is applicant claiming to be the first to impregnate a fertilizer with a solution of a herbicide dissolved in an organic solvent. Nor is applicant claiming to be the first to dissolve prodiamine and other herbicides in N-methyl pyrrolidone. Rather, applicant is claiming to be the first to discover that the explosion risk inherent in conventional technology for combining prodiamine with particulate

fertilizers can be essentially eliminated without adverse impact on health or the environment by adopting a solution/impregnating approach using N-methyl pyrrolidone as the solvent.

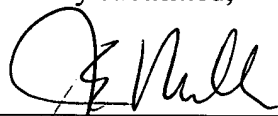
For the reasons explained in the Request for Reconsideration filed on June 30, 2006, a *prima facie* case of obviousness has not been established because the prior art fails to suggest using a solvent/impregnating approach for combining prodiamine with particular fertilizers. For the reasons explained above, the prior art also clearly fails to suggest the unexpected result that applicant found as a result of adopting this approach in the particular manner claimed, i.e., that the explosion risk inherent in conventional technology could be eliminated by proceeding in this manner. Therefore, the present invention, as now claimed, is unobvious and patentable.

If any additional fees are due, please charge our Deposit Account No. 03-0172.

Respectfully submitted,

Date

1/8/07

  
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## Assessing the Risks of Combustible Particulate Solids

### Introduction

Combustible solids such as Barricade 65 MC are characterized by a variety of measures that derive from safety testing.

Particulate solids are initially tested to determine if they will combust when dispersed in air and when consolidated as a thin layer of powder. If combustible, the explosion violence is determined in a spherical reactor. A test is performed to determine the lowest amount of spark ignition energy required to initiate a dust explosion.

Other tests are performed, but these are core tests to characterize the hazardous results from a spark ignition of combustion.

### Combustibility Testing

Powder is added to a vertical tube in which there are electrodes through which an electric spark is passed. A switch activates a burst of compressed air to blow the dust into a cloud and the spark is released. If there is combustion, then it is obvious the powder will burn as dispersion in air. Barricade 65 MC combusts.

A strip of powder is formed on a plate in a triangular cross-section. An electrically heated wire at 1000°C is pressed to one end of the powder strip. A rating scale is used to calibrate the burning behavior of the consolidated solid. The scale is given in the table.

Test Result		Class	Reference Substance
No ignition	No spreading of fire	1	Table salt
Brief ignition, rapid extinction		2	Tartaric acid
Localized combustion or glowing with practically no spreading		3	D+ Lactose
Glowing without sparks (smoldering) or slow decomposition without flames	Fire spreads	4	8-amino-1-naphthol-3, 6-disulfonic acid
Burning fireworks or slow quiet burning with flames		5	Sulfur
Very rapid combustion with flame propagation of rapid decomposition without flame		6	Black powder

A Barricade 65 MC powder strip at 100°C temperature is rated 2.

### Maximum Violence of an Explosion

Spherical reactors either 1 cubic meter in volume or 20 liters volume are used to test for the maximum explosion violence.

M. J. Nelson  
Feb. 19, 2002

This is the test of the gas liberation and exothermic heat effects from the combustion, i.e., explosion, reaction. Testing is done this way because there may be more than one fuel present and the reactions that occur may not go to completion.

The approach is to directly test the combustion reaction for a worst credible case situation, beyond that which would occur in practice. The results can then be used as the measure to scale a safety response. Most actual dust explosions have less violence than the worst case tested.

Testing is done with different quantities of powder put into the "bomb." This is done to have different dust cloud concentrations produced when an initial blast of compressed air enters the bomb when the test begins. A chemical igniter is used to provide the ignition source. The test that gives the greatest violence is that used to present the results.

The violence of the explosion is given by a maximum pressure rate of rise with time expressed in units of [bar\*meter / second]. There can also be a class rating. The table below gives the ratings.

Dust Explosion Class	Kst <sub>max</sub> [bar * meter/ sec]
St = 1	> 0 – 200
St = 2	201 – 300
St = 3	> 300

Barricade 65 MC is an St = 2 dust, the Kst = 265 bar \* meter / sec.

The other part of the measure of the explosion violence measurements is the maximum pressure developed over the initial pressure. Initial pressure is usually atmospheric pressure. The units are bars gauge [bar = 14.5 psi]. Most dusts have a Pmax of 10 bars gauge or less. Barricade 65 MC is at the upper range.

Barricade 65 MC has a Pmax of 10.2 bars gauge.

#### Minimum Ignition Energy

Minimum ignition energy is measured in an apparatus much like that cited above for dust combustion testing. The spark at the electrodes is predetermined to produce a particular quantity of energy by use of prewired circuits. The measurement is discrete and not continuous.

Tests are made with different amounts of powder added to produce different dust cloud concentrations. Normally a parabola-shaped curve is produced when ignition energy as the ordinate is plotted against the dust concentration. The parabola goes through a minimum that is presented as the minimum ignition energy.

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Feb. 19, 2002

Normally the dust concentration that produces the experiment with the least energy requirement is high, such as 750 grams per cubic meter. Light cannot pass through such a dense cloud.

The "MIE" result is presented as a range of values. The low number is below the amount of energy that can ignite the cloud and the upper number of energy is either the minimum ignition energy or greater than the minimum energy.

For Barricade 65 MC there have been two recent tests. One test reported:  $3 \text{ mJ} < \text{MIE} \leq 10 \text{ mJ}$  and the other test reported  $1 \text{ mJ} < \text{MIE} \leq 3 \text{ mJ}$ .

### Resistivity

Volumetric resistivity of powder is measured in an apparatus that applies an electrical voltage to one end of a sample volume of powder and measures the current that passes through the volume. The resistance at these conditions is calculated. Resistivity is a component of resistance, as in the formula:

$$R(\text{resistance, ohms}) = l(\text{length, meter}) * \rho(\text{resistivity, ohm} * \text{meter}) / V(\text{volume, meter}^3)$$

Simply stated, if the electrical resistivity in ohm-meters is  $10^{10}$  or larger, the powder is called non-conductive. Conductive powders can be electrically charged flowing through non-conductive conduits and if the charge is not drawn away by bonding and grounding, the residual charge is available for immediate and complete release. Non-conductive powders can be electrically charged flowing through either a conductive or non-conductive conduit. The charging hazard can be controlled by electrically bonding and grounding and choice of equipment that is electrically conductive (metals rather than plastic).

Barricade 65 MC can be electrically conductive. One test reported a resistivity of  $1.48 * 10^7 \text{ ohm} * \text{meters}$  (conductive) whereas another test reported a resistivity of  $2 * 10^{13} \text{ ohm} * \text{meters}$  (non-conductive). All test were done in atmospheres of low relative humidity, about 38 %. When high relative humidity is present, the water in air helps make the powder heap's outer surface more electrically conductive. Resistivities lower and the powder heap becomes more conductive. Two tests at 66 % relative humidity report resistivities of  $4.8 * 10^3 \text{ ohm} * \text{meters}$  and  $6.3 * 10^4 \text{ ohm} * \text{meters}$ .

An article from Chemical Engineering Progress magazine is a good summary of testing as well as practice. It is a more complete description of particulate solids' safety.



***A REPRINT FROM***

**A REPRINT FROM THE JUNE 1999 ISSUE OF**

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# Chemical Engineering Progress

**PREVENT EXPLOSIONS OF  
COMBUSTIBLE DUSTS**

Norbert Jaeger  
Richard Siwek

Please note in equation 2 on p. 29 there is a typographical error. The equation should be:

$$[V(m^3)]^{1/3} * dP/dt(bar/s) = K_{max}(bar * m / s)$$

# Prevent Explosions of Combustible Dusts

*If not treated properly, dust layers and clouds of combustible materials can wreak havoc in the plant due to static discharges. However, testing for combustion ratings and following some basic rules will help to prevent problems.*

Norbert Jaeger,  
Ciba Specialty Chemicals  
Richard Siwek,  
FireEX

available  
**on-line**  
[www.aiche.org](http://www.aiche.org)

**T**o sufficiently survey the potential danger of a dust, an engineer is normally forced to carry out numerous laboratory tests that are based on standardized methods. The results are known as safety characteristics (Table 1). Depending upon the effort spent, a more or less comprehensive picture will result, revealed as a mosaic. The scope of the tests has to be determined in close collaboration between the tester and user, working toward the solution of the problem.

Here, we will review these tests, and then show how to apply the results to set up handling procedures that will promote safety. Tests are made for both dust layers and dust suspensions, since these show different behavior. Transforming the safety characteristics to plant conditions is certainly the key for safe operation.

## DUST LAYERS Ignition rating

An unknown product should not initially be tested in large quantities. The following is used at Ciba Specialty Chemicals as a screening test. A small sample (approximately 100 mg) of a dry product is exposed to a hot plate at different temperatures. A reaction is considered to have taken place at a given temperature if the test sample shows any of the following within 5 min: *ignition with flames, emission of sparks, red hot glow, or spontaneous decomposition without fire*. The ignition properties of the product are classified with a rating on the basis of the

ignition temperature level (Table 2). Data from this simple test are only good enough to describe the flammability behavior at a specific temperature.

## Combustion rating

This test measures the ignitability and the combustibility of a dried product according to the following criteria:

- Can the product be ignited at all?
- Is the ignition propagated?
- Is there a fire or a flameless reaction?

The tests are carried out in a ventilated laboratory hood. The air velocity is approximately 0.2 m/s. The superimposed low-velocity air stream is necessary to vent the inert gases generated upon ignition that may inhibit the combustion behavior of the dust (Figure 1) (1).

If the combustibility is needed at an elevated temperature (e.g., an anticipated drying temperature), the test can be performed in a drying oven with a guaranteed air supply (1). By increasing the dust sample to an overall length of 25 cm (10 in.), the same test procedure can be used to classify a product as a readily combustible solid of Division 4.1 in accordance with the U.N. "Recommendations on the Transport of Dangerous Goods," (2) if the burning rate exceeds a certain limiting value.

The combustibility of the product is rated in accordance with the course of the reaction and characterized as a class number according to VDI (Table 3). A temperature increase from 20° to 100°C normally results in a change of the burning class (BC) from 1-3 to 4-6.

### Exothermic reaction in an air stream

This test determines the temperature of a product in a hot air stream, in which an oxidation reaction occurs at a significant scale. The test is used for products that are subjected to elevated temperatures in an air stream for a short time period, such as in a spray or fluid-bed dryer. This test allows the dryer's inlet temperature to be set.

The term "autoignition" means the ignition of combustible matter in air subjected to uniform heat. The temperature of the surrounding atmosphere (storage temperature) that initiates autoignition after self-heating of the product is called the autoignition temperature. Self-heating is caused by an already evident oxidation in air at the storage temperature. Such oxidation will liberate a certain amount of heat per unit time and mass. If the heat is not entirely transmitted to the surroundings, the product will heat up and autoignition may result.

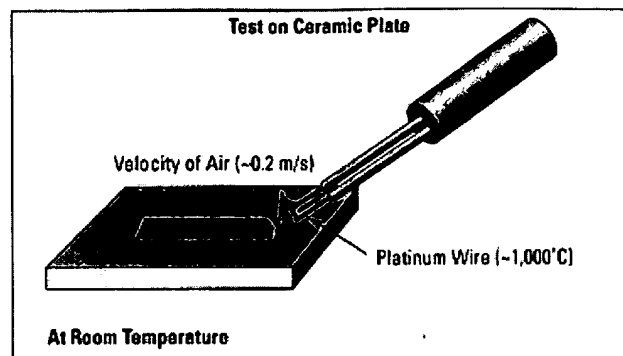
The autoignition temperature is determined in a Grever oven (Figure 2). A test material (approximately 8 mL) is placed into a stainless steel wire-mesh container and put into the oven. A second container, filled with a reference material (graphite), is also inserted. Air is blown through a heating block. An exothermic reaction is considered to occur if the temperature curve of the test substance rises above that of the graphite. The test reports gives the temperature at which the first exothermic reaction occurs (3).

### Open-cup test for exothermic decomposition (Luetolf)

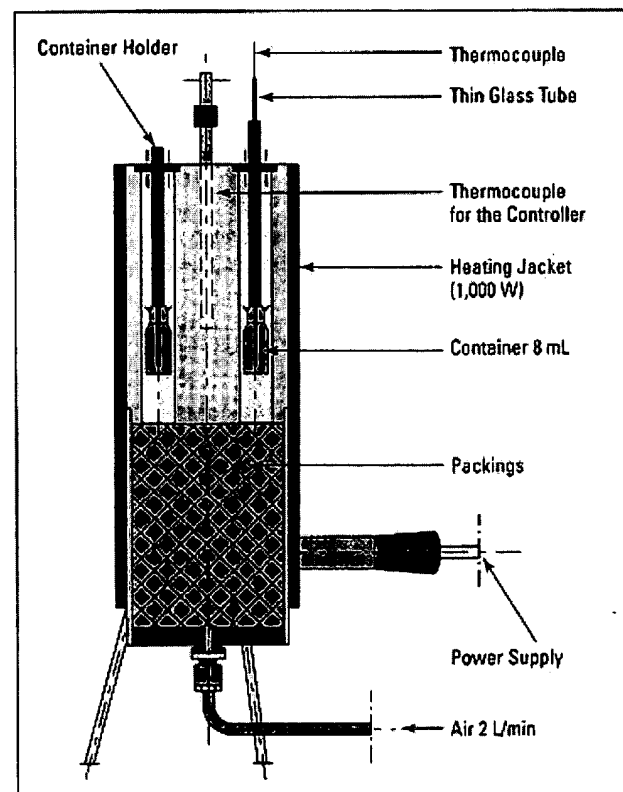
Elevated temperature may cause a product to undergo a chemical transformation that will not require oxygen. The reaction may be endothermic or exothermic. The latter greatly affects safety, while the former may only affect operations or quality control.

Exothermic reactions may generate gases upon decomposition. These increase the pressure in a closed ves-

■ **Figure 1.** The combustion rating is determined at ambient temperature.



■ **Figure 2.** Grever oven detects an exothermic reaction in an air stream.



sel. In addition, these gases may be flammable. This could pose an additional explosion risk.

Determining an exothermic decomposition in an open cup (Figure 3) involves measuring the lowest temperature that results in an exothermic reaction in a test tube under lean oxygen conditions. This test is made on products or reaction mixtures subjected to elevated temperatures over long periods, closed off from fresh air. Examples include reactors, and vacuum ovens and dryers (3).

### Temperature-programmed conditions (dynamic test)

A test sample and a reference sample (again, graphite) are heated in test tubes at a rate of 2.5°C/min, up to a final oven temperature that depends upon the sample. For distillation residues and products to be milled, the maximum is 350°C, while it is 220°C for final products that are dried during manufacture.

A linear plot of temperature vs. time will reveal a straight, sloped line for the graphite, and, for the sample, a

**Table 1. Safety characteristics of dust layers and dust clouds.**

Dust Layers	Dust Clouds
Ignition rating	Lower explosible limit (LEL)
Burning class (BC)	Maximum explosion overpressure $P_{max}$
Constant temperature stability (CTS)	Maximum explosion constant $K_{max}$
Differential scanning calorimetry (DSC)	Limiting oxygen concentration (LOC)
Exothermic reaction in a fresh air stream (Grewer)	Minimum ignition energy (MIE)
Exothermic decomposition in an open cup	Minimum ignition temperature (MIT)
Shock sensitivity	

**Table 2. Ignition-properties classification for dust layers based ignition temperature level.**

Result	Rating
No reaction at 360°C (possible at higher temperature)	1
Reaction at 360°C	2
Reaction at 330°C	3
Reaction at 300°C	4
Reaction at 270°C	5
Reaction at 240°C	6

peak above this line will show an exothermic reaction. The onset temperature for this reaction is at the point at which the temperature-time exotherm rises above the line for graphite.

In addition to the above-mentioned procedure, the following tests can be done simultaneously: a flammability

test of the decomposition gases; and a procedure measuring the amount of gases.

#### Constant temperature stability (isoperibolic) test

A sample is stored in an oven at constant temperature for 8 h, and its temperature-time profile is recorded. If an exotherm exists, the sample temperature will rise and peak above the oven reading. If a peak is found, fresh samples are tested and the oven temperature is dropped in 10°C-increments until no temperature rise is found. Thus, the minimum exothermic temperature is found.

#### Hot storage test

In many products, exothermic processes (decompositions) may take place at relatively low temperatures, with a low reaction velocity and a low heat-generation rate. If a material

is discharged at an elevated temperature and stored in large, compact quantities, heat dissipation may be reduced so much that self-heating takes place. Often, this process is slow initially, but, then, with rising temperature, it can accelerate within hours or days and finally change into a thermal explosion, rupturing the container and autoigniting the product.

The hot storage test determines the lowest temperature at which, under insulated conditions, a substance shows an exothermic reaction. This test is carried out under almost adiabatic conditions.

The sample is placed in a 200-mL Dewar flask and stored in a laboratory oven at constant temperature for up to 72 h. If an exothermic reaction takes place, the sample temperature will rise, especially in the center of the flask. The test is repeated with fresh samples at lower temperatures — again, in steps of 10°C — until self-heating is less than 5°C over the oven temperature. This temperature is the Dewar temperature limit (DTL). There is a linear correlation between the adiabatic induction time of a detected decomposition and the oven temperature at a constant volume.

To allow for the difference of scale between the Dewar flask and a 1.5-m<sup>3</sup> receiving container used in the test, and to provide for an adequate margin of safety, the maximum discharge temperature MDT is fixed at:

$$MDT = DTL - 50^{\circ}C \quad (1)$$

#### Differential scanning calorimetry (DSC)

In addition, DSC can determine the onset temperature and quantify the total energy release  $\Delta H$  of any exothermic reaction. This test is done in addition to the hot storage one.

#### Shock sensitivity

For grinding processes and paddle dryers with bars, the sensitivity of a product to shock has to be found. A product is impact-sensitive and explosive if it disintegrates with a bang

**Table 3. Test results determine the burning class (BC) of a powder layer.**

Test Result		Class	Reference Substance
No ignition	No spreading of fire	1	Table salt
Brief ignition, rapid extinction		2	Tartaric acid
Localized combustion or glowing with practically no spreading		3	D+ lactose
Glowing without sparks (smoldering) or slow decomposition without flames	Fire spreads	4	H- acid*
Burning fireworks or slow, quiet burning with flames		5	Sulfur
Very rapid combustion with flame propagation or rapid decomposition without flames		6	Black powder

upon its exposure to impact under given test conditions. A test sample is placed between the upper and lower parts of a stamp (Figure 4). Then, a drop hammer is ejected. This test is carried out in a dark room to observe any kind of reaction. The result is regarded as positive if the sample burns or decomposes with detonation, flame (sparks), or heavy smoke (1, 3).

## DUST CLOUDS

Any time a combustible dust is processed or handled, a potential for deflagration exists. The degree of the deflagration hazard will vary depending on the type of combustible dust and processing methods. Evaluating a combustible dust explosion hazard and the necessary prevention techniques employed are determined by using test data as described below (4).

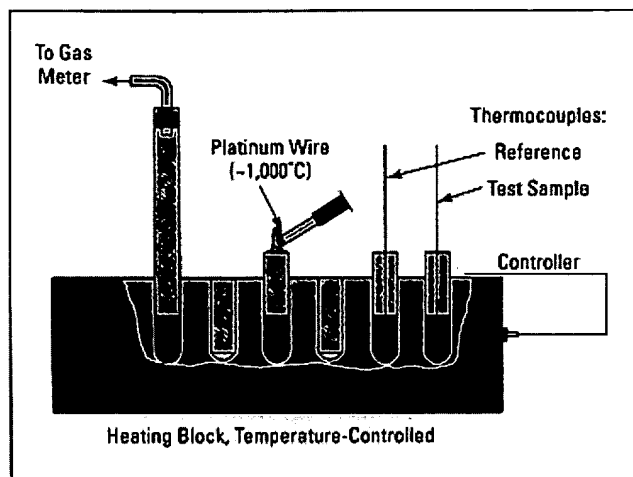
### Modified Hartmann apparatus

This test is designed as a qualitative pretest of the explosion behavior of dust/air mixtures. A test sample is placed in a 1.2-L cylindrical glass tube (Figure 5). By introducing pressurized air into the glass chamber, the dust is blown through an ignition source (a continuous spark with an electrical energy of about 10 J).

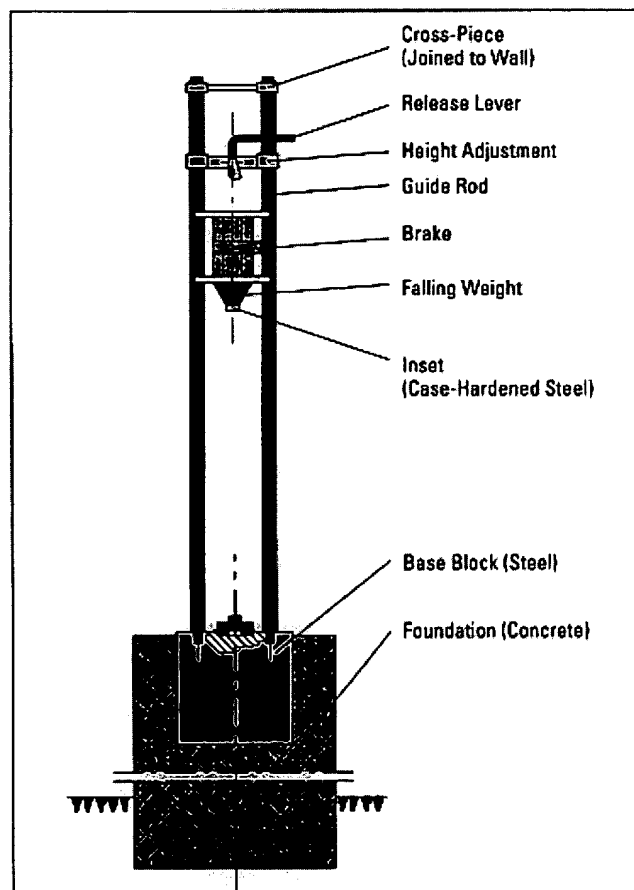
A positive reaction is recorded if a dust fire occurs, or if the test equipment's hinged cover opens. As a rule of thumb, only dust explosions leading to an indication 1 in the apparatus are true St 1 dusts. (The St scale, shown in Table 4, will be explained later.) Otherwise, for St 0 and 2, additional tests must be made in a Siwek 20-L apparatus.

### Siwek 20-L apparatus

This method measures the deflagration parameters of a combustible dust/air mixture in a near-spherical 20-L (or greater) closed vessel — the Siwek apparatus. The parameters are the dust explosivity, lower explosion limit (LEL), maximum explosion overpressure  $P_{max}$ , maximum explosion overpressure constant  $K_{max}$ , and the limiting oxygen concentration (LOC) (3, 5–7).



■ **Figure 3.** Lutefof oven evaluates exothermic-reaction temperatures for materials exposed to heat for long periods at lean oxygen concentrations.



■ **Figure 4.** Falling hammer test measures sensitivity to shock, important in operations such as grinding.

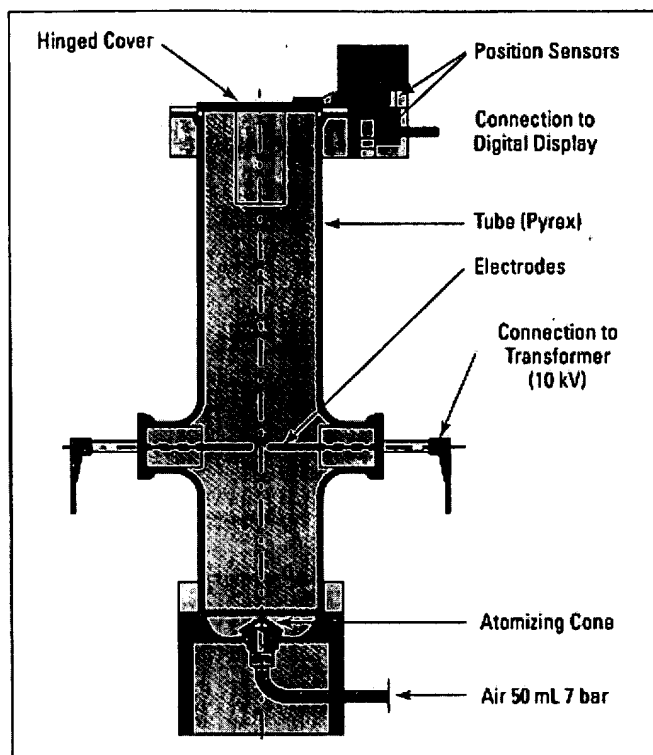
The test uses chemical igniters as the ignition source; the ignition energy (IE) is 10 kJ, and the ignition delay time  $t_i = 60$  ms.

The parameters measured are  $P_{max}$  and the maximum rate of pressure rise  $(dP/dt)_{max}$  (Figures 6 and 7). This

test provides information to predict the effects of an industrial-scale deflagration of a dust/air mixture.

$P_{max}$ , when determined in closed, spherical, or cubic vessels of sufficient volume ( $V \geq 20$  L) with a central ignition source, is practically indepen-

■ **Figure 5.**  
Modified  
Hartmann device  
makes qualitative  
pretests of dust/air  
mixtures.



dent of the volume of the vessel. But,  $(dP/dt)_{max}$  does depend on the volume. It decreases with increasing volume, following the cubic law.  $K_{max}$  is dust- and test-method specific, but independent of volume. The cubic law is applicable only for a volume  $V \geq 20$  L.

The cubic law is:

$$V^2 [m^3] \times (dP/dt)_{max} [bar/s] = K_{max} [m-bar/s] \quad (2)$$

The large number of dusts produced and handled in processing plants led to a classification of dusts, according to their  $K_{max}$  values, into dust explosion classes (Table 4).

**Table 4. How dust explosion classes are defined.**

Dust Explosion Class	$K_{max}$ m-bar/s
St 1	> 0-200
St 2	201-300
St 3	> 300

### Minimum ignition energy (MIE)

For an assessment of the hazard situation in dust processing plants, knowledge of the minimum ignition energy is indispensable. This value can conceivably establish the extent and, hence, the cost of protective measures (4). Finding the minimum ignition energy involves testing for the failure to ignite (4, 8). The MIE of a combustible substance is the lowest value of the electrical energy stored in a capacitor, which upon discharge, just suffices to ignite the most readily ignitable fuel/air/mixture at atmospheric pressure and room temperature. Various test apparatuses are used worldwide to determine the MIE. To assure a standardized test procedure, a third-generation test apparatus known as MIKE 3 (Figure 8) was developed by Kühner AG, Switzerland.

The MIE is usually quoted as a range: The lower value represents the highest energy at which no ignition is found in at least 10 experiments. The higher value, on the other hand, is the lowest energy at which the dust/air mixture is just ig-

nited: No ignition < MIE < Ignition.

Finding the MIE is described in a standard of the International Electrotechnical Commission (IEC) (9), and in an ASTM standard soon to be published (10). The MIE is generally obtained with an inductance in the discharge circuit. However, to assess the incendivity of electrostatic discharges in dust/air mixtures, the MIE must also be determined without an inductance in the discharge circuit. With flammable gases, the influence of the inductance is generally not detectable. Dusts, particularly very easily ignitable dusts, also exist where the inductance has also no influence.

Tests should be conducted with dust clouds of optimum dust concentration for ignition and having the lowest turbulence level experimentally attainable. The optimum dust concentration cannot be obtained in one step. Therefore, a special procedure is required. Its main steps are:

1. Start with a value of the ignition energy that will reliably cause ignition of a given concentration in air of the dust. Then, reduce the spark energy in steps (e.g., halving it) at the given dust concentration until the dust cloud no longer ignites at 10 tests at a given energy.

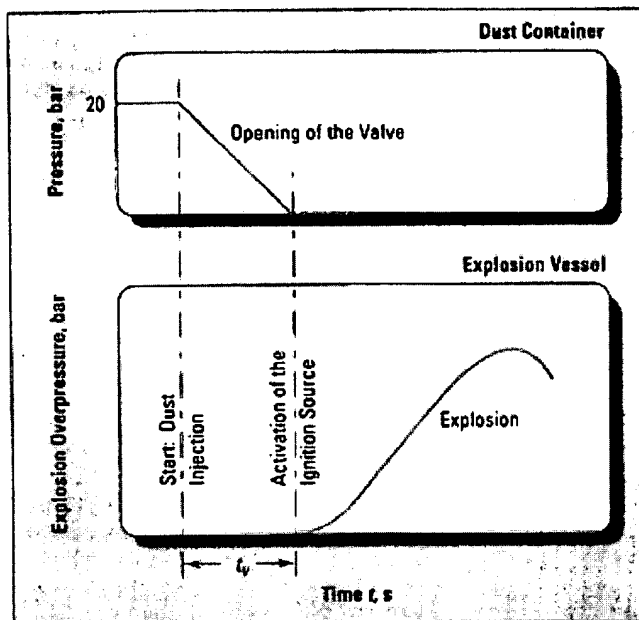
2. Repeat the procedure at different dust concentrations until the lowest MIE is found.

The MIE lies between the highest energy at which ignition fails to occur in 10 successive attempts to ignite the dust/air mixture  $W_1$ , and the lowest energy at which ignition occurs within 10 successive attempts  $W_2$  (Figure 9):

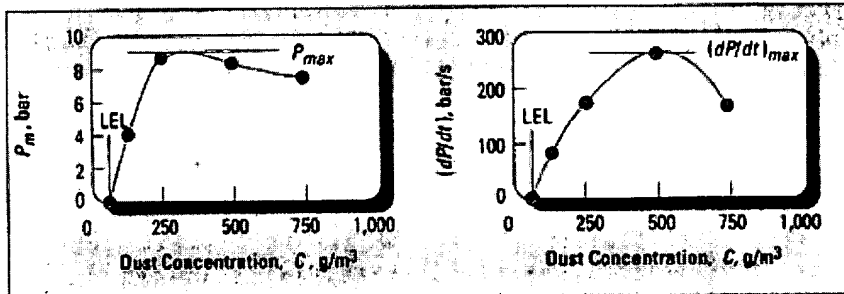
$$W_1 < MIE < W_2 \quad (3)$$

Inductance  $L$  causes the capacitor to discharge in a protracted manner. As Figure 10 shows, dust/air mixtures are more readily ignited by time-extended discharges than by purely capacitive discharges. The three symbols in the figure represent experiments made at laboratories of different companies.

■ **Figure 6.** Results of a dust-investigation procedure done in standard test equipment.



■ **Figure 7.** Determination of maximum explosion pressure and maximum rate of pressure rise.



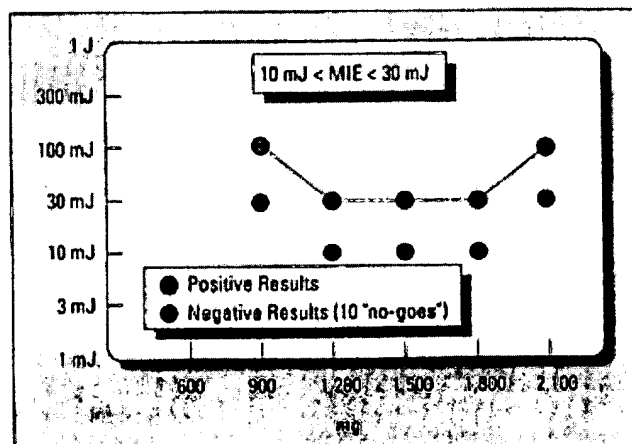
If the MIE is used to assess ignition hazards resulting from electrostatic charges, it must be found without an inductance in the discharge circuit. Only in this way is it possible to make a realistic evaluation of the incendivity of electrostatic discharges in dust/air mixtures.

## Minimum ignition temperature (MIT) of dust clouds

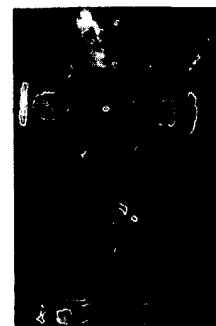
This MIT is the minimum temperature at which a dust cloud will autoignite. The cloud is exposed to air and heated to various temperatures in a furnace (11). Ignition is indicated by visual observation of a flame. The chemical nature of the dust, as well as its concentration, particle size, moisture, and surface area all affect the result. The MIT can be determined either in the Godbert-Greenwald (GG) fur-

nace (Figure 11a) or the BAM furnace (German Federal Institute for the Testing of Materials (Berlin), Figure 11b). To compare the MIT values measured in both furnaces, these minimum temperatures have been investigated for

■ **Figure 9.** Results of a typical test showing boundaries for the MIE.



■ **Figure 8.** Apparatus for finding the minimum ignition energy (MIE) of dusts.



over 100 dusts from various laboratories (5, 9). The following equation, found by regression analysis, compares values measured by both furnaces:

$$MIT_{GG} = 1.1 \times MIT_{BAM} - 10^\circ C \quad (4)$$

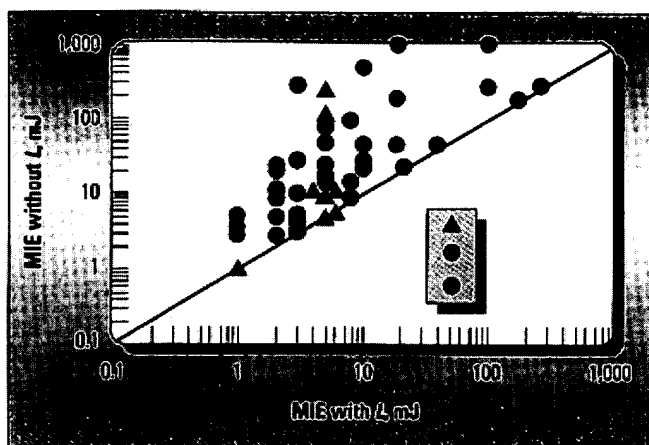
## Powder volume resistivity

A material's powder volume resistivity  $\rho_R$  characterizes its static dissipative properties. Surfaces of materials will be polluted if exposed to the air, and will consequently adsorb humidity. Resistivity is not an absolute property of a powder, but depends strongly on its moisture content and on the method of measurement. From an electrostatic point of view, dusts are considered to be conductors incapable of storing charge until their resistivity exceeds  $10^9 \Omega\cdot m$ .

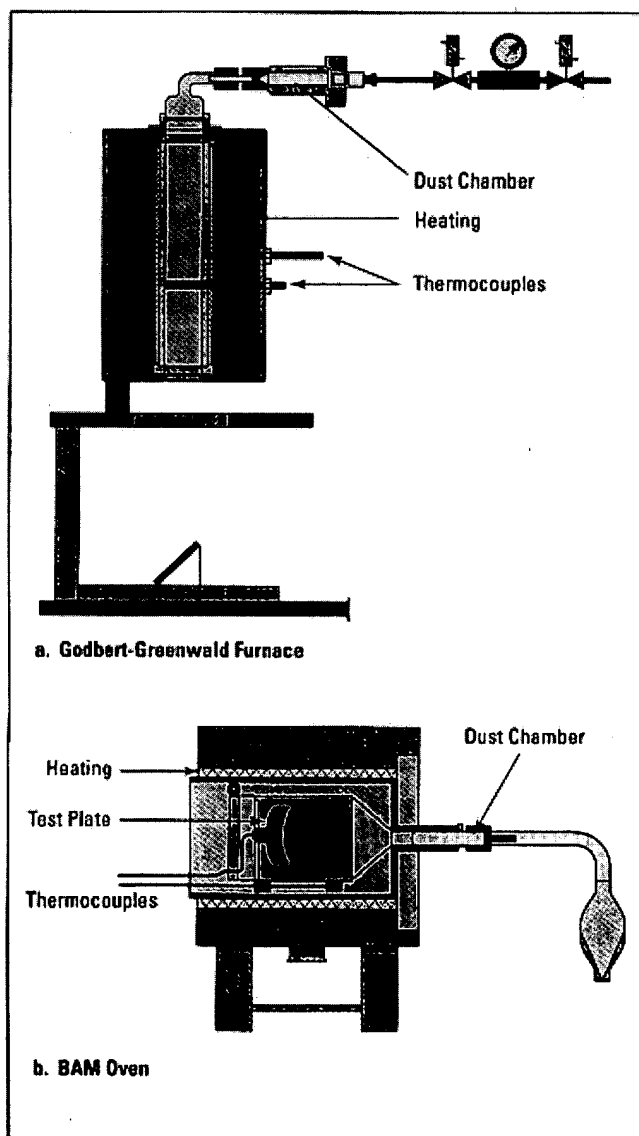
## Test requirements

Where no safety data are available, the required tests must be done before introducing a product into a process.

■ **Figure 10.**  
Dust/air mixtures  
are more readily  
ignited by  
time-extended  
discharges than  
by purely  
capacitive  
charges.



■ **Figure 11.**  
MIT of dust  
clouds is  
measured in  
one of two  
furnaces.



The test laboratory must repeat the requisite tests whenever local management suspects that an operation has become more hazardous. This may increase as a result of:

- Modifications in the production process (including preparatory steps) or equipment substitutions;
- Irregularities during production; and
- Changes in the manufacture or quality of any raw or auxiliary materials.

Due to changes in governmental laws, international regulations, and testing technologies, the specific tests should be repeated at least once every five years.

## Outlook

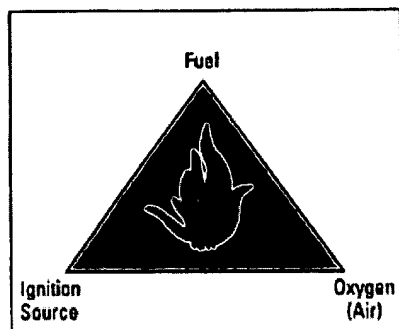
Thorough knowledge of the ignition behavior of dust/air mixtures with electrical sparks (MIE) and hot surfaces (MIT) is important for assessing the hazards in dust-carrying plants. The ignition behavior essentially sets the extent, and, hence, the cost of the protective measures to be used. This is especially true for the prevention of ignition sources and for the understanding of the ignition phenomena regarding static electricity, e.g., brush discharges, bulk surface discharges, spark discharges, and propagating brush discharges.

## PROTECTIVE MEASURES

Using preventive measures against explosions requires reliably excluding one of the three requirements necessary to generate an explosion, as shown in the familiar hazard triangle (Figure 12), that is, eliminating at least one of the sides of the triangle (12). An explosion can, thus, be excluded with certainty by:

- Avoiding the development of explosible mixtures (combustible dusts, flammable gases); or
- Replacing the atmospheric oxygen by an inert gas, working in a vacuum, or using inert dust; or
- Preventing the occurrence of effective ignition sources.

All three measures fall under what



■ **Figure 12.** The familiar hazard triangle serves as the basis for explosion protection.

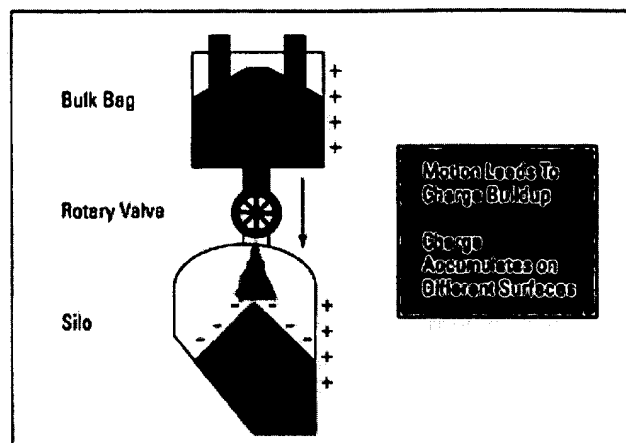
is called preventive explosion protection. For safety, the engineer must ensure that at least one of the three conditions is eliminated or so strongly reduced that an explosion is no longer possible (8, 12-14).

When combustible dusts are handled, avoiding an explosive atmosphere by keeping the dust concentration outside the explosive range is rarely possible, due to sedimentation or whirling up of the material. Thus, as a matter of principle, an explosive atmosphere can only be avoided with certainty by reducing the oxygen concentration, *e.g.*, inerting. In practice, however, inerting often cannot be used. For such situations, the only measures become either avoiding effective ignition sources or using explosionproof equipment.

It is acceptable to avoid effective ignition sources as the sole protective measure, if it is established that the occurrence of these ignition sources is excluded with certainty under all normal operating conditions, as well as for all possible deviations. "Trivial" ignition sources (such as welding or smoking) must be excluded by administrative actions.

This article does not look at ignition sources that could result from processes introducing energy into the product being handled, such as from mechanically generated sparks or hot surfaces. Nor does it discuss products that may form glowing particles during handling (*e.g.*, those with a BC  $\geq 4$  (see Table 3)).

■ **Figure 13.** Filling and emptying operations can pose a serious electrostatic hazard if the powder is combustible.



Electrostatic charging is certainly an ignition source not to be underestimated in powder operations. This is a normal occurrence in most such processes and operations, and, therefore, our main topic. As such, we will indicate protective measures. In understanding these measures, the following product and plant properties are keys for an accurate hazard assessment:

- MIE of the bulk material (measured without inductance in the discharge circuit);
- MIT of the bulk material;
- $\rho_R$  of the powder;
- Particle-size distribution of the bulk material and its median value  $M$ ; and
- Volume and shape of the silo or container (volume and shape of the product heap and of the dust cloud).

Unless otherwise stated, the following sections are based on the assumption that the bulk materials are handled without flammable gases or vapors being present.

## Filling and emptying operations

In these operations, ignition hazards are of prime importance owing to electrostatic charging. The hazards comprise possible charge accumulation not only on equipment, as well as on drums and containers, but also for bulk materials that are insulating (Figure 13).

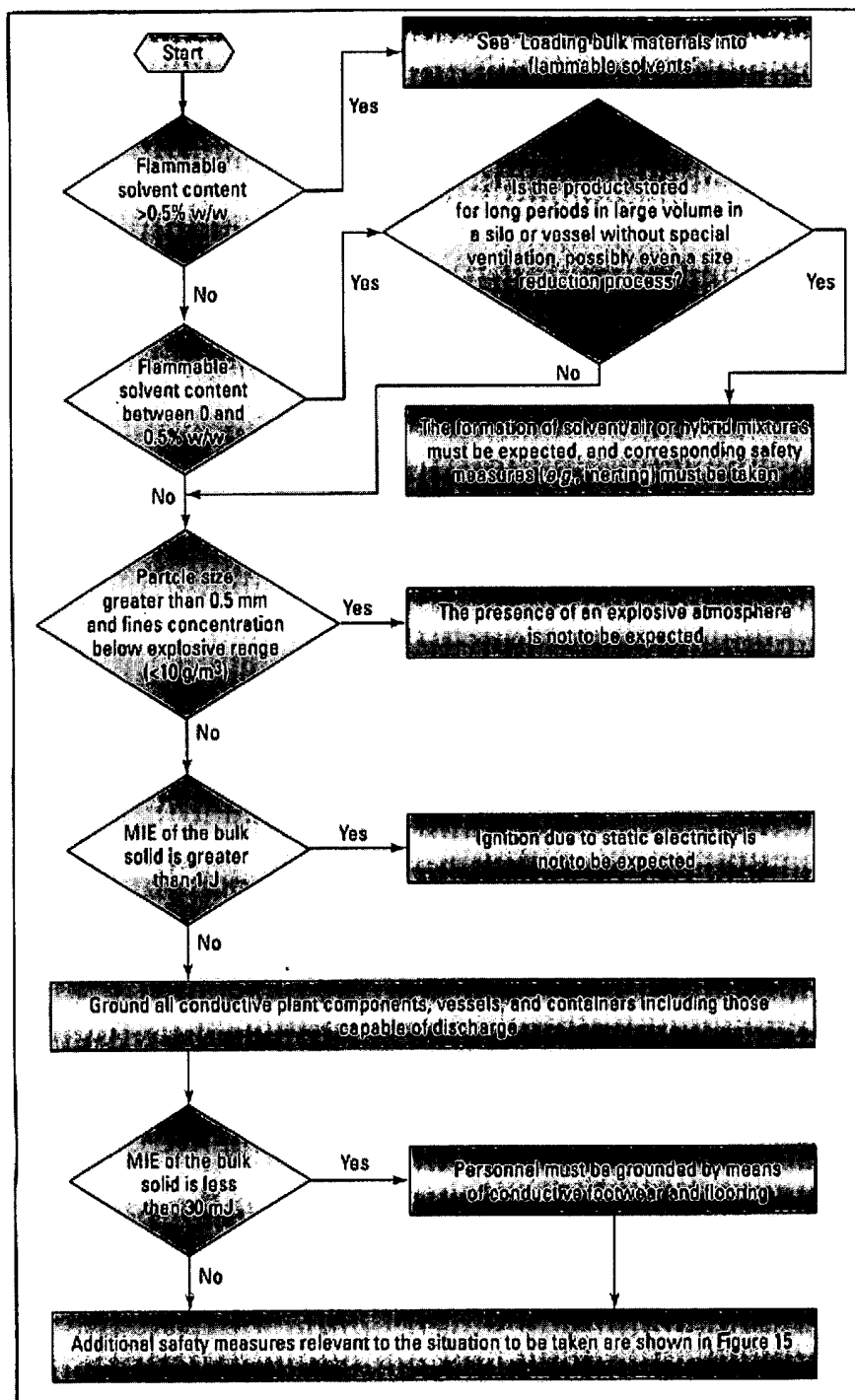
Assuming that the insulating bulk material carries a charge, filling repre-

sents the most hazardous operation for the following reason: During this procedure, the material undergoes dispersion (via gravity feed, pneumatic transport, or by some other means) and can, therefore, acquire charge during the separation processes occurring in transport. The bulk material and, hence, its associated charge, are then packed into a small space. Here, the charge is not able to flow to the ground quickly enough, even with a conductive and grounded receiver. This generates a high space-charge density and electric field. In addition to charge accumulation, there can be problems due to heat accumulation and the possibility of entrainment of smoldering lumps.

To help ensure safety, a decision tree is presented for safe handling, based on the product and plant properties listed above (Figure 14). Use this decision tree, along with matrixes in Figure 15 to ensure safe filling and emptying of containers, vessels, and silos of varying volumes.

## Loading bulk materials into flammable solvents

Whenever it is possible, bulk materials should be fed into flammable solvents under closed conditions and in an inert atmosphere (Figure 16). This can be accomplished by using a bucket wheel, two-valve system, feed screw, or by conveying by an inert gas. If such a closed introduction system is not possible, the next best thing is either to cool the solvent below its flash point (at least



■ **Figure 14.** Follow this decision tree to help prevent fires and explosions from occurring with combustible powders in your plant.

by 5°C) before loading the bulk material, or to introduce the bulk material first and then the flammable solvent.

If it is unavoidable for the open addi-

tion of a bulk material into a previously loaded flammable solvent at a temperature less than 5°C below flash point, then the following points must be considered:

- The operator must be grounded;
- All aids to introduction, such as funnels, charging chutes, and the like, must be made in conducting materials and be grounded during transfer;
- Containers for solvent and powders must be of conductive material and grounded during the charging process;
- Conductive vessels for solvents and bulk materials may be used with an insulating internal coating up to 2 µm maximum, if they are grounded during filling and emptying; and
- Normal loose plastic sacks or plastic liners should not be used. Plastic liners or plastic sacks with at least a one-sided nonchargeable surface (surface resistance of  $<10^{11} \Omega$  at 30% relative humidity) are allowed according to ASTM D257-93(1998) (15) (e.g., plastic sacks with an antistatic coating, paper sacks, or paper sacks lined on one side with a normal plastic coating, if the coating thickness is less than 2 mm).

## Mixing

Provided that the following conditions are met, effective ignition sources during mixing generally do not occur, even with dusts exhibiting high ignition sensitivity:

- During filling and emptying of the mixer, the considerations and measures that apply are the same as those for the same operations in containers;
- In the filling and emptying of the mixer, the mixing elements must be at a standstill or run at a circumferential speed (relative speed) that does not exceed 1 m/s. This restriction must be assured by technical safeguards;
- In the closed condition and with a fill level of 70 vol. % or more, the circumferential speed of the mixing elements is no longer restricted;
- No insulating inner coatings with high electrical breakdown-strength (breakdown voltage must be less than 4 kV) may be affixed to the inner wall of the mixer (product buildup must be checked);
- Circumferential speeds up to 10 m/s can be tolerated during filling and emptying with a mixer not filled to 70 vol. %, provided that the MIT of the

		Minimum Ignition Energy, MIE, mJ (without inductance)				
		<3	3-10	10-30	30-1,000	>1,000
Specific Powder Resistivity, MΩ-cm	<1 Conductive	A: Ignition of the dust particles must be conductive and grounded. B: A conductive container capable of discharge and grounded.				
	Any Value					
	<0.5	No additional measurement requirements other than those from Method B, Part Two (Figure 16).				
	>1 (Non-conductive)	No additional measurement requirements if the material is stored by gravity from a conductive and grounded installation. or B: The material filling must be 5 kV or higher conductive and dischargeable (500 pF) charged container that is grounded. or A: For additional measurement requirements, see Part Two (Figure 16).				
	Median Particle Size, mm					
	0.5-1.5					
	1.5-3.0					
	3.0-6.0					

- Use only conductive containers, 1 MΩ (<10<sup>6</sup> Ω), or those capable of discharge and ground.
- † Containers capable of discharge: The leakage resistance to the ground point from any point on the surface of the container must be less than 100 MΩ (<10<sup>8</sup> Ω).
- ‡ Charge dissipative (≥10<sup>8</sup> ≤ 10<sup>11</sup> Ω) containers having at least on one side a surface resistance  $R_{SA}$  measured according to ASTM method D257-93 (Surface Resistivity) of less than 100 Giga Ω (10<sup>11</sup> Ω) at 30% relative humidity and more than 100 MΩ at 65% relative humidity.

Figure 15a. For volumes of less than 0.2 m<sup>3</sup> (55 gal).

processed product lies above the limit values specified in Table 5; and

- Mixers that have an orbiting, rotating helical screw inside of a conical shell with bottom support of the screw can heat up during operation, so care must be exercised with substances capable of spontaneous decomposition.

Table 5. MIT lower limits for products filled and emptied in mixers while running.

MIE*, mJ	MIT, °C
< 1	Do not process
1-3	530
3-10	500
10-30	465
30-100	430
100-300	395
300-1,000	360
> 1,000	325

\* The MIE values must be determined with an additional inductance in the discharge circuit.

### Dust separation

The dust explosion hazard must not be underestimated in dust separators, especially filters. The probability is large of a fine dust atmosphere sensitive to ignition. In addition to the entrainment of ignition sources, which must be assessed based on the product properties (e.g., formation of smoldering lumps) and upstream op-

eration, the danger of ignition through electrostatic charging is of prime importance (Figure 17).

Electrostatic charging must be inhibited by the following measures:

- Grounding of all conductive apparatus parts. If a filter cloth made of insulating material is used, particular attention must be paid to grounding all conductive parts that could possi-

Table 6. Requirements for safe use of FIBCs.

Bulk Material MIE	No Explosible Atmosphere	Explosible Dust or Vapors	Flammable Gases
MIE* > 1 J	A	B	C
3 mJ < MIE* < 1 J	B	B	C
MIE* < 3 mJ	C	C	C

\* Measured without inductance in the electrical circuit

Key:

A: No special requirements.

B: Breakdown voltage of the FIBC wall material must not exceed 4 kV to prevent propagating brush discharges.

C: The bag material including the slings must be electrostatically conductive. The resistance to the ground measured at any bag location (inside and outside) must be less than 100 MW (10<sup>6</sup> W). The FIBC must have a grounding tap. The conductivity and the necessity for grounding must be clearly marked.

		Minimum Ignition Energy, MIE, mJ (without inductance)							
		<3	3-10	10-30	30-100	100-300	300-1,000	>1,000	
Specific Powder Resistivity, MΩ-m	<1 Conductive	Any Value	- All parts of the equipment must be conductive* and grounded. - All containers must be conductive* or dischargeable† and grounded.						
		<0.1	No additional measures required other than the ones from the decision tree (Figure 14).						
		0.1-0.2							
		0.2-0.5	No additional measures are required if the material is charged by gravity from a conductive and grounded installation. or Restrict the filling rate to 5 kg/s and use conductive* or dischargeable†/charge dissipative‡ container that is grounded. or Apply additional explosion protection measures (e.g., inerting). Otherwise: Seek advice of experts.						
		0.5-1.0							
		1.0-2.5							
		2.5-5.0							
	>10,000	<0.1	§						
		0.1-0.2	No additional measures are required if the material is charged by gravity from a conductive and grounded installation.	§					
		0.2-0.5		§	No additional measures required other than the ones from the decision tree (Figure 14).				
		0.5-1.0		§					
		1.0-2.5			§				
		2.5-5.0	Apply additional explosion protection measures if the fines are in concentration of greater than 10 g/m <sup>3</sup> . or Seek advice of experts.				§		

\* Use only conductive containers, 1 MΩ (<10<sup>6</sup> Ω), or those capable of discharge and ground.

† Containers capable of discharge: The leakage resistance to the ground point from any point on the surface of the container must be less than 100 MΩ (<10<sup>8</sup> Ω).

‡ Charge dissipative (≥10<sup>8</sup> ≤ 10<sup>11</sup> Ω) containers having at least on one side a surface resistance R<sub>SA</sub> measured according to ASTM method D257-93 (Surface Resistivity) of less than 100 Giga Ω (10<sup>11</sup> Ω) at 30% relative humidity and more than 100 MΩ at 65% relative humidity.

§ Fines in concentrations greater than LEL are not to be expected for dust-free forms during normal discharge or charging operations involving packaging.

■ Figure 15b. For volumes of 0.2 – 2.0 m<sup>3</sup> (55 – 550 gal).

bly be insulated from the ground (e.g., filter supports, clamps). This must be especially checked after repair and maintenance work;

- With a MIE < 3 mJ or in the presence of flammable gases or vapors in the air being cleaned, electrically conducting filter materials must be used, except when inerting is employed. Continuity of the conductivity and safe grounding must be checked. Multiple washings can have an adverse effect on the continuity of the filter material's conduc-

tivity and, thus, require repeat checking; and

- All inner walls on which dust can impact at high speed must not have any insulating inner coatings with a high electrical breakdown-strength (breakdown voltage must be less than 4 kV; check these periodically).

In general, with dusts with a MIE < 10 mJ, it is advisable either to implement explosion protection measures that go beyond the avoidance of effective ignition sources or consult company specialists. Further, the fan

must be installed on the clean air side and dust deposits must be avoided in the pipe and fan housing (check periodically or install a dust control unit).

### Flexible intermediate bulk containers (FIBCs)

FIBCs are used on ever-increasing scale in the powder handling industry. Depending upon the hazard situation where they are used, they must meet different requirements (Table 6) to avoid ignition hazards caused by electrostatic charging.

		Minimum Ignition Energy, MIE, mJ (without inductance)		
		< 10	10 - 1,000	> 1,000
Specific Powder Resistivity, MΩ-m	< 1 Conductive	Any Value	<ul style="list-style-type: none"> <li>All parts of the equipment must be conductive* and grounded.</li> <li>All containers must be conductive* or dischargeable† and grounded.</li> </ul>	No additional measures required.
	1 - 10,000	<ul style="list-style-type: none"> <li>All parts of the equipment must be conductive* and grounded.</li> <li>All containers must be conductive* or dischargeable** and grounded.</li> <li>Apply additional explosion protection measures (e.g., inerting), or Seek advice of experts.</li> </ul>	<ul style="list-style-type: none"> <li>Use only conductive* or dischargeable† containers that are grounded.</li> <li>or</li> <li>Restrict the filling rate to 5 kg/s.</li> <li>or</li> <li>Apply additional explosion protection measures (e.g., inerting), or Seek advice of experts.</li> </ul>	
	> 10,000	<ul style="list-style-type: none"> <li>Apply additional explosion protection measures (e.g., inerting), or Seek advice of experts.</li> </ul>	<ul style="list-style-type: none"> <li>Use only conductive* or dischargeable† containers that are grounded and</li> <li>Apply additional explosion protection measures (e.g., inerting), or Seek advice of experts.</li> </ul>	

\* Use only conductive containers, 1 MΩ (<10<sup>6</sup> Ω), or those capable of discharge and ground.  
 † Containers capable of discharge: The leakage resistance to the ground point from any point on the surface of the container must be less than 100 MΩ (<10<sup>8</sup> Ω).

Figure 15c. For volumes of > 2.0 m<sup>3</sup> (550 gal).

Most FIBCs on the market today are made of polypropylene ribbon fabric. To pass the Type B classification, the following requirements are recommended:

- Any inner polyethylene coating or liner present must not be thicker than 20–30 μm; and
- The inliner must not be made of plastic.

FIBCs meeting the requirement of Type C are constructed as one of the following:

- The basic fabric consists of conductive material (e.g., plastic with a sufficient admixture of carbon); or
- The basic fabric consists of nonconductive material, but the web contains interwoven threads of conductive plastic material that are interconnected; or

- The basic fabric consists of nonconductive material, but the web contains interwoven metal threads that are interconnected; or

- The basic fabric consists of nonconductive material, but the FIBC has an internal conductive coating.

To meet the specification as a Type C bag, the following requirements are recommended:

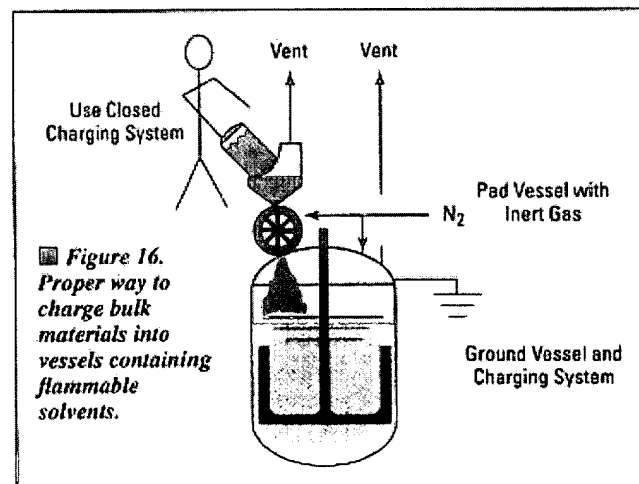
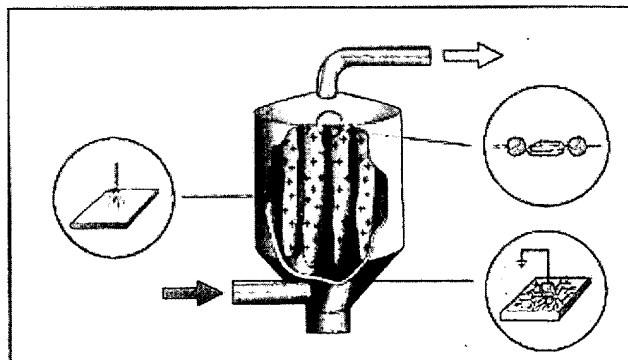


Figure 17. Electrostatic ignition sources can plague a dust collector.



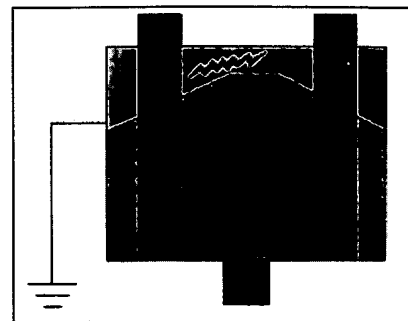
- The FIBC must have an indication of its conductivity and the grounding requirement during charging and discharging;

- The FIBC must have a clearly marked area for the attachment of the grounding clamps; and

- The lifting straps must also be

made of conductive material and have a leakage resistance of less than  $10^8 \Omega$  to the FIBC body.

Using a Type C bag requires permanent grounding of the bag during the whole period while the bag is filled or discharged (Figure 18). The discharge from an ungrounded bag aligns to a sin-



■ Figure 18. Electrostatic discharges from a permanently grounded Type C FIBC.

gle discharge point. Such a discharge is strong enough to ignite dust clouds.

The generated charge in the product pile cannot fully dissipate to the ground. Small discharges can occur along the surface of the pile. These are too weak to ignite dust clouds if the volume of the bag is less than  $2 \text{ m}^3$ , but strong enough to ignite solvent vapors.

CEP

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## **Trip Report: LESCO, Sebring Manufacturing Plant; Monday, March 4, 2002**

### **Introduction**

Russ Kahn and Mel Nelson of Syngenta visited the Sebring, Florida manufacturing plant of LESCO on Monday, March 4, 2002. We were guests of LESCO's Paul Ferrell. Our purpose was to provide sales support to Syngenta's Jerry Pauley concerning potential sales of Barricade™ 65 MC, a crabgrass herbicide.

LESCO manufactures a "weed and feed" product that uses a competitor's herbicide. The competitive product is an organic solution containing the active ingredient. Syngenta's Barricade™ 65 MC is a finely divided powder. The concern by LESCO personnel is the powder is combustible and can be ignited with a small amount of energy under the most favorable conditions for combustion.

The plant visit provided an opportunity to review the LESCO process to formulate their weed and feed product and evaluate the safety aspects of introducing Barricade™ 65 MC. This report and a previous discussion with LESCO's Sebring personnel are concerned with generally recognized safety practices used when processing combustible particulate solids. The context of these discussions concerns practices Syngenta would undertake in processing Barricade™ 65 MC and other combustible solids. These ideas are offered to LESCO so they may evaluate whether they find them appropriate to incorporate into their process.

### **Properties of Barricade™ 65 MC**

Literature concerning general practices of safe handling of combustible particulate solids and safety test properties of Barricade™ 65 MC were previously transmitted by e-mail to LESCO. The two MICROSOFT Word files transmitted are: (1) Prevent Explosions of Combustible Dusts by Jaeger and Siwek.doc, and (2) Assessing the Risks of Combustible Particulate Solids (Barricade).doc.

Barricade™ 65 MC has a small risk of thermal degradation reactions and a possible risk of explosions due to its low minimum ignition energy (MIE) at conditions most favorable to combustion. Barricade™ 65 MC can be and is formulated by customers to produce final products in a safe manner when the appropriate measures are put into practice.

Barricade™ 65 MC is blended with the fertilizer portion of the product and is present at less than two weight percent when uniformly mixed. At these low concentrations, the properties of the weed and feed product are those of the fertilizer portion rather than Barricade™ 65 MC.

### **LESCO Process for Herbicide Addition**

Not all of LESCO's raw materials are known; however, were Barricade™ 65 MC included in the weed and feed product, the following would hold.

Various constituents of the fertilizer component of the product are blended prior to introduction of Barricade™ 65 MC. Barricade™ 65 MC would be added and blended into the fertilizer due to turbulence present in a blending screw conveyer [See photo 6 below]. Barricade™ 65 MC is added to the blending screw conveyer by gravity falling from the discharge of a smaller screw conveyer [See photo 5 below] used to meter herbicide addition.

The small herbicide addition screw conveyer takes feed from a small accumulation vessel [See photos 4 and 5 below] located at a higher elevation. Herbicide enters the accumulation vessel from an unloading station [See photos 1 and 2 below] located above. Gravity is used to move solids between consecutive pieces of equipment.

Presently the unloading station is made to manually dump bags of about 20 kilograms size. A grill is placed horizontally over an inverted hollow pyramid. At the inverted apex of the pyramid is the discharge chute that passes solids into the small accumulation vessel. Above the grill are sidewalls and a dust capture opening to contain dust that may be released. A duct connects to the dust capture opening and eventually terminates at a dust collector [See photos 7 and 8 below] that is used to capture fugitive dust from other locations in the process.

LESCO personnel indicate the present herbicide unloading station could be replaced with an unloading station made to accommodate flexible intermediate bulk containers (FIBCs) or “big bags”. Subsequent to the LESCO site visit it was learned Barricade™ 65 MC is not now packaged in “big bags”.

## Analysis

### Fugitive Dust Collector

This dust collector is a typical design in which filter bags are mounted on frames made of metal wire welded together in the shape of a long cylinder. The dust collector's dusty air plenum is separated from the filtered air plenum by a sheet of metal. Holes are made in the plenum-separating sheet. Filtered air from the bags passes through these holes.

A snap-ring is used to attach the filter bag at the hole opening in the metal sheet that separates the two plenums. There is a mating ring in the edge of the hole that accepts the ring of the bag. A flexible metal ring is sewn into the bag that allows the ring to be compressed to allow entrance into the mating ring.

The metal parts associated with the filter bag that do not have direct electrical contact with the electrically grounded dust collector body are the snap ring and the filter bag frame. The concern is for ungrounded metal parts that can become electrically charged through a process called induction. Powder that passes through the duct to the dust collector can become electrostatically charged

through the multiple brief contacts with duct walls. Charged powder rests on the filter fabric surface and the accumulated charge of the powder has an effect on the metal of the frame and snap ring that are in close proximity. The metal parts are isolated from the grounded metal of the dust collector by the filter fabric. There can be a high resistance path to the flow of electricity through the fabric, but over multi-minutes to hour-long periods, there is a flow of electricity. The charge of the powder repels the like charge on the metal so if negatively charged powder was on the filter the metal would be positively charged.

Present practice is to remove dust captured by the filter bags once a day, probably by reverse air blowing and maybe by mechanical agitation. The concern is a dust cloud is created at the time of bag cleaning of possibly a sufficiently high concentration to require only a small amount of ignition energy to explode. The jostling of the bag assemblies from cleaning may be sufficient to move the metal parts close enough so they are able to electrically discharge through a spark to a grounded part of the dust collector.

The hazard is a matter of probability. If enough of the powder in the dust collector is Barricade™ 65 MC or a blend of other combustible dusts and the dust cloud is of sufficient concentration at the location where a spark is generated, then there could be a dust explosion. It could be a period of years before all the separate requirements are produced all at the same time.

At the Syngenta St. Gabriel plant the dust collectors have a different design to attach the bags. On the dusty air side (bottom part) of the plenum-separating sheet are attached short nozzles that match in diameter the hole size in the sheet. These nozzles are the mounting brackets to which the filter bags and metal support frames are attached. The bag and frame assembly is slipped over the mounting nozzle and held in place with a clamp that looks like an automobile hose clamp.

At St. Gabriel the concern for ungrounded metal parts associated with the filter bags is handled through a modification of the bag. Two electrical conductors made of a weave of fine wires are sewn into the bag. At the open mouth of the bag a conductor is sewn so that one part of the conductor is on the bag outside and the remaining length is sewn on the inside. In side view the conductor looks like the letter "U" with the fabric in the open space of the letter.

When a filter bag is mounted on the metal frame the longer length of the bag is folded inside the frame. Then when the bag and frame are mounted on the mounting nozzle and held in place with a clamp, all metal parts are electrically bonded together by the woven conductors. The mounting nozzle grounds the whole assembly.

As an added measure, the electrical resistance from frame to body of the dust collector can be measured to assure there is bonding. This method removes the

ignition source from the combustion (fire) triangle of fuel, oxidizer and ignition source.

LESCO may consider the use of a conductor sewn into the top of their filter bags to ensure all the metal parts are bonded together and connected to the body of the dust collector.

#### Charging of Barricade™ 65 MC to Process

Bags (in the range of 20 kilogram size) are manually dumped into the existing unloading hopper

The potential hazard comes from the worker manually emptying bags. When the worker wears shoes with high electrical resistance soles, he is isolated from earth ground. There is the possibility of a static charging mechanism when powder slides by the bag surface and powder slides by powder. Charges on the bag can charge the worker. If the worker touches a grounded part of the unloading station when a sufficiently dense cloud of Barricade™ 65 MC is present, there could be ignition.

For ignition to happen, there needs to be: (1) Ambient air with a sufficiently low relative humidity to make not effective alternate discharging paths to ground over the worker's body and shoes. A surface coating of water makes a conductive pathway. (2) The worker does not touch a grounded conductive part of the structure or equipment to discharge himself away from the presence of a dust cloud. (3) The dust cloud is of sufficient density at the location of the worker's discharge spark to be ignitable by the energy released.

Protective measures are to: (1) Have a conductive tether attached to both ground and the worker, usually at the waist or wrist. (2) Have conductive shoe soles and a clean standing surface so the worker is grounded as he stands. Usually the conductive tether is used, as it is difficult to keep the standing surface clean.

#### Bonding, Grounding and Non-conductors

Ungrounded conductors of electricity that become charged are potential ignition sources should they come close enough to a grounded conductor that a spark discharge occurs. Precautions should be taken to prevent ungrounded conductors when combustible powders are present.

Bonding is the electrical connection of separate electrically conductive parts such as pieces of ducting or parts of equipment. Grounding is the electrical connection to earth of electrically conductive parts that previously were not connected to the earth.

A high quality method to assure all conductive parts are bonded together is to have electric wire without insulation attached to individual parts where they abut each other. Visual checks that all pieces are connected with wires gives a highly reliable assurance bonding is achieved for those locations where combustible powders are present.

Non-conductive ducting lengths and metal ducts with manufacturer-applied coatings thicker than two milli-meters are not desirable. There is a phenomenon called a propagating brush discharge that occurs when there are high rates of powder flow through non-conductive flow passages where a metal part or wall is close to the outer duct surface or the duct outer surface is wetted with water. The Sebring plant did not appear to have the possibility of this phenomenon during the inspection. If we should return to the Sebring plant, then the likelihood of this hazard will be looked for more closely.

The undesirable effect of use of non-conductive ducting and gaskets are their use may allow conductive duct pieces to not be bonded and grounded [See photo 3 below].

#### Circumferential Speed of Moving Parts

Internal company research developed a methodology to prevent mechanical sparks from being an ignition source. Tramp metal contacting a fast moving metal part can create a mechanical spark for which there is a low probability of ignition.

For Barricade<sup>TM</sup> 65 MC, the maximum circumferential velocity to preclude the possibility of a mechanical spark is one meter per second.

The two screw conveyers mentioned at the start of this report are locations where there are internal moving parts which may be exposed to high concentrations of Barricade<sup>TM</sup> 65 MC powder. The small metering screw turns so slowly that on inspection cannot be close to a speed of one meter per second. The mixing screw is about nine inches in diameter and turns at 47 revolutions per minute. The circumferential velocity is about 0.56 meters per second.

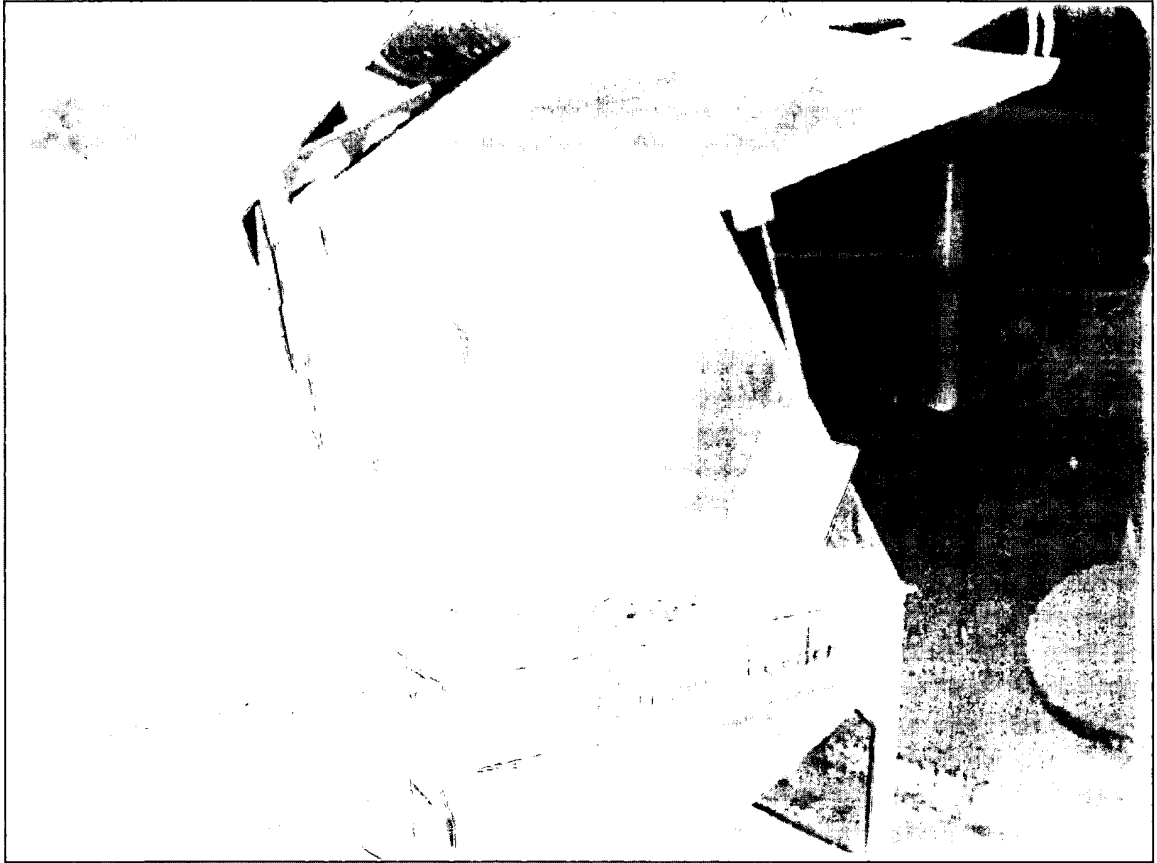
There was another rotating device located in the body of the vessel that feeds the small metering screw. The vessel is shown in photo no. 5 below. Speed of the tips of the rotating part was not determined at the time of the plant visit.

LESCO personnel should review the circumferential speed information to confirm its accuracy.

#### Photographs of LESCO Sebring Unit to Manufacture Weed and Feed Product

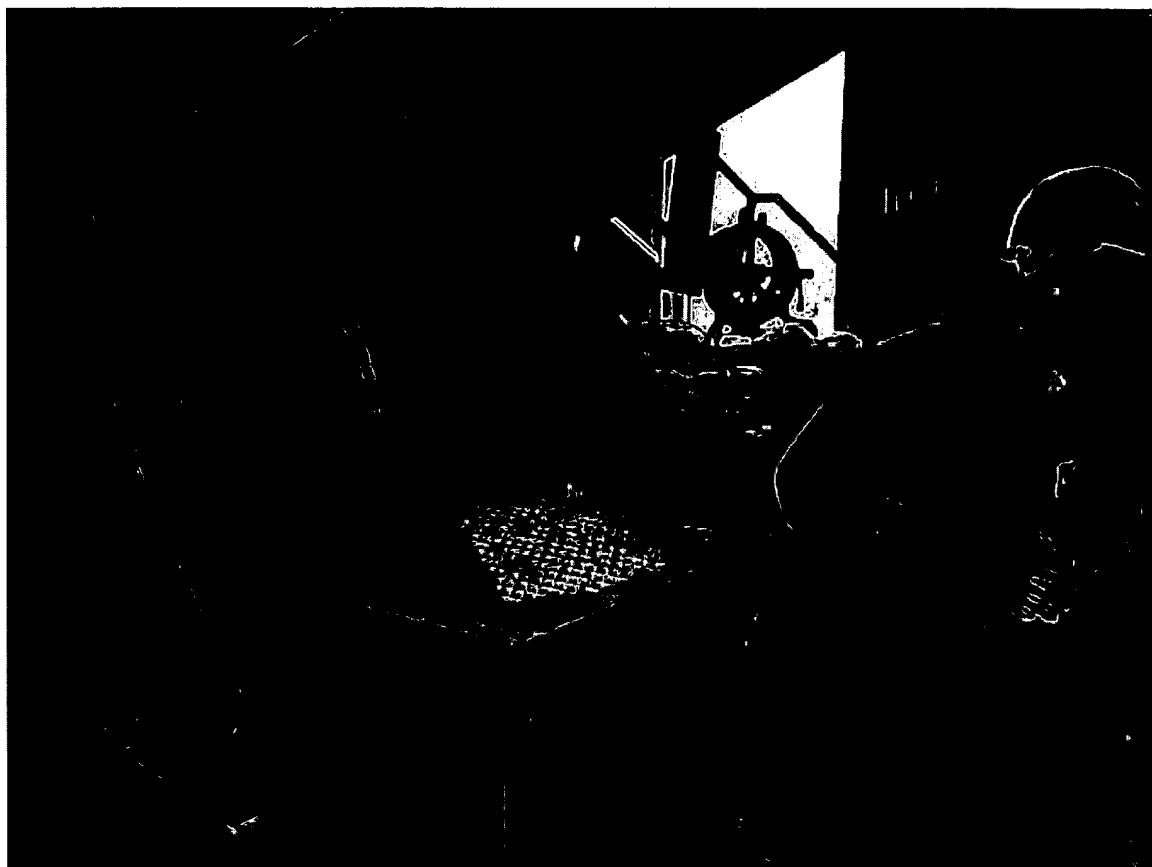
Personnel from the Sebring plant took photos of their unit and shared them with us. We thank the LESCO people for their assistance.

Photo No. 1



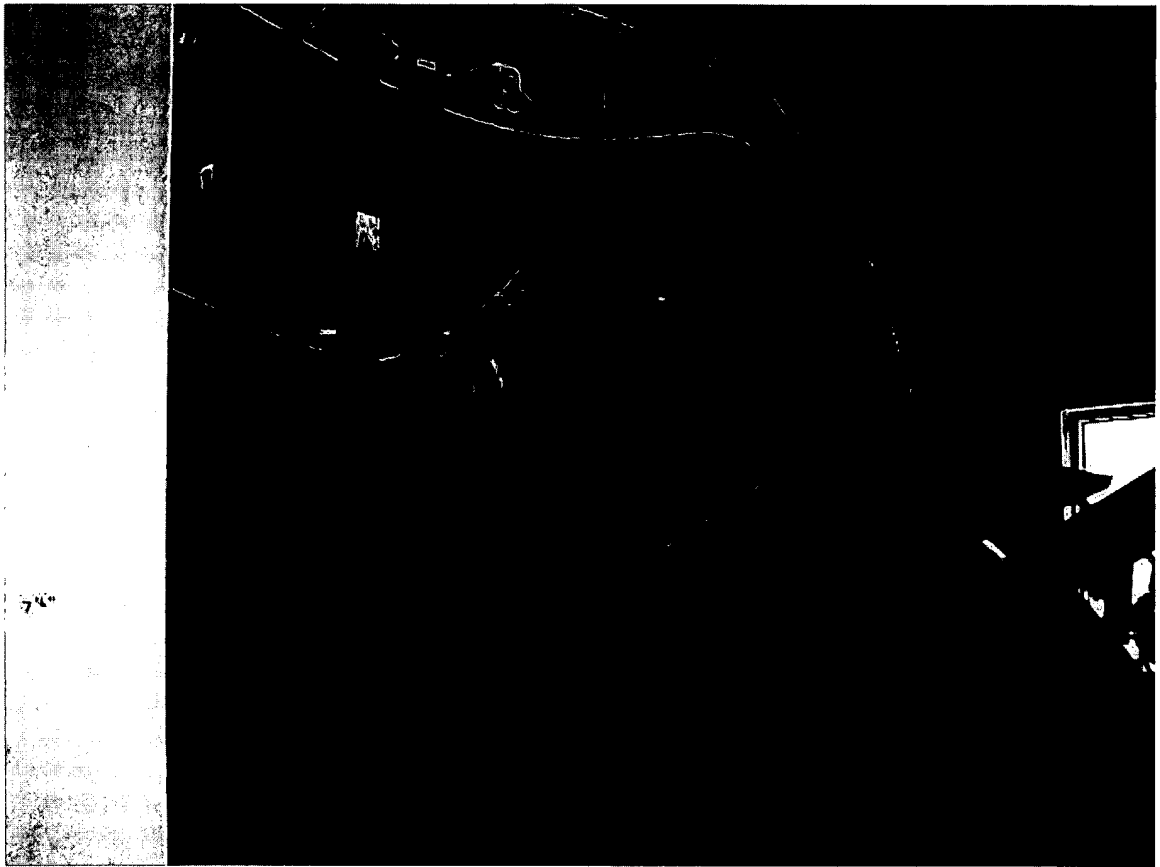
The photo above is the present unloading station where individual bags are emptied in to the process. A fugitive vent opening is in the back wall.

Photo No. 2



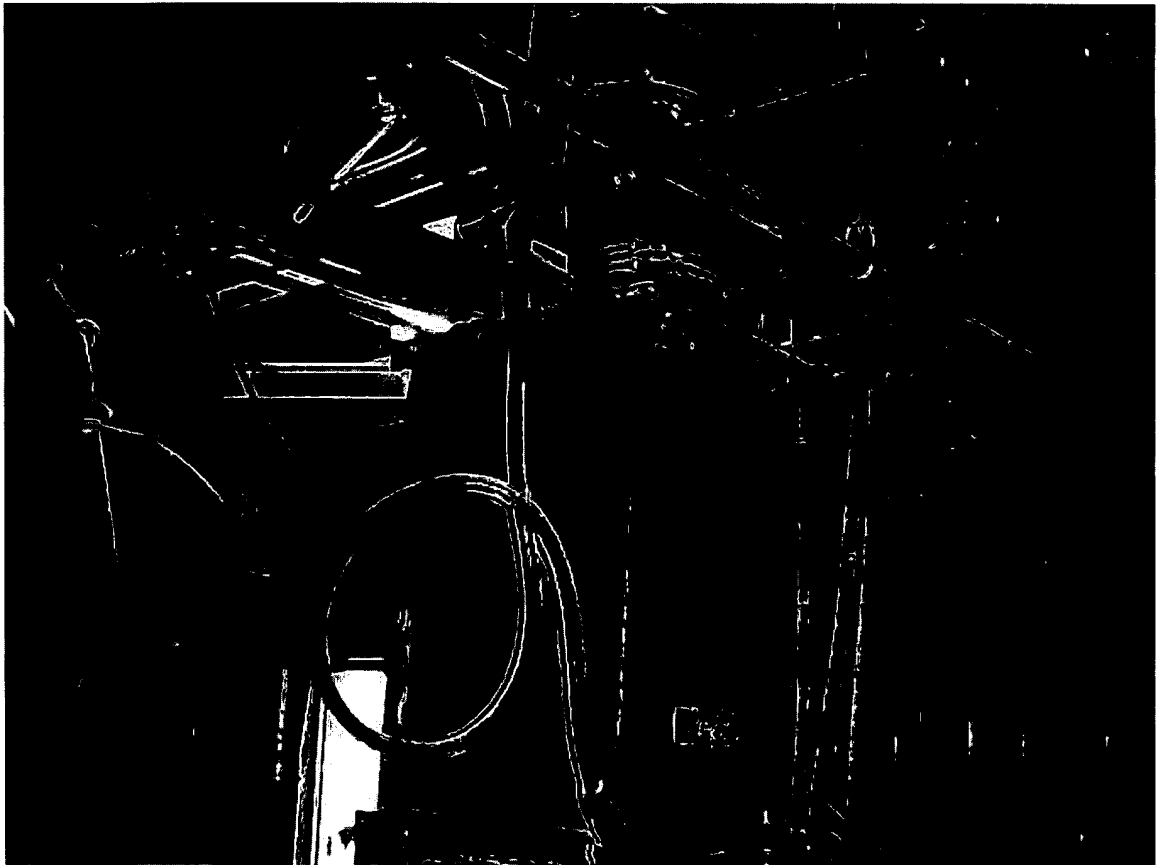
A second view of the bag unloading station, with a view of the bottom pyramid-shaped outlet.

Photo No. 3



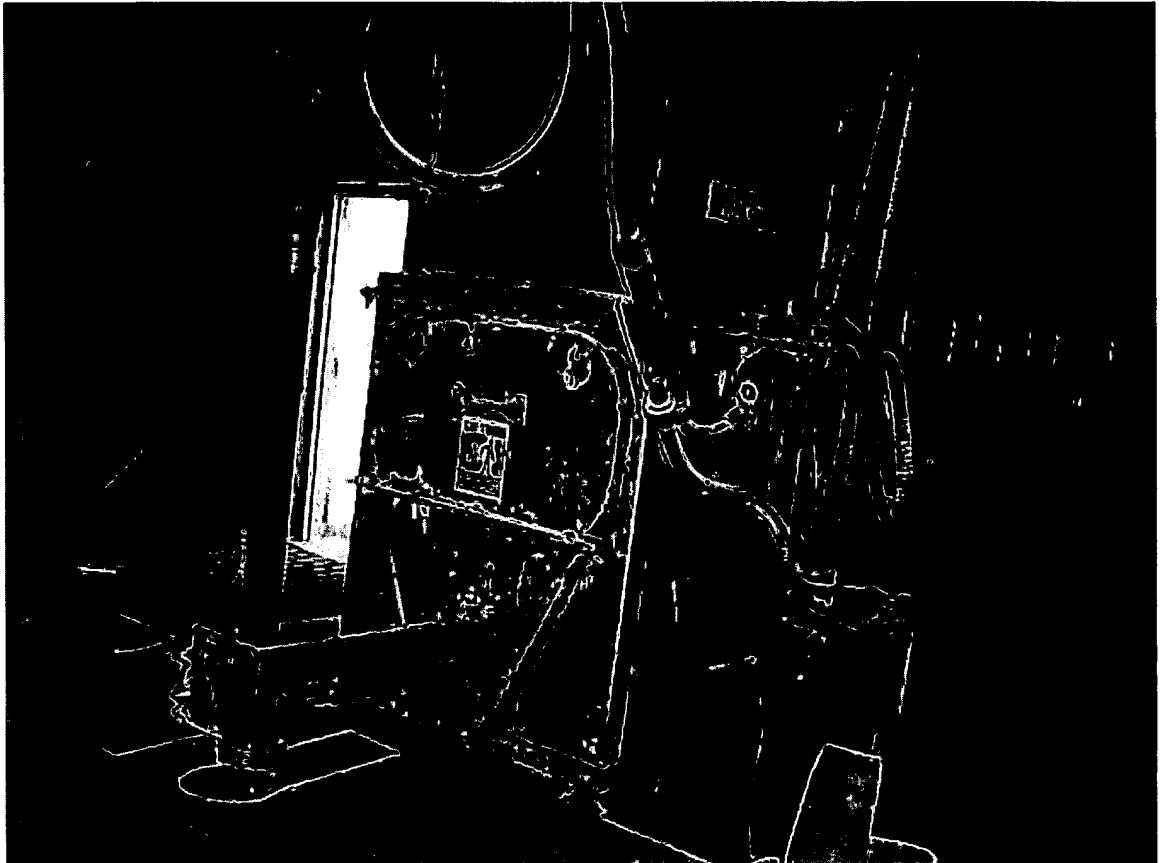
View of ducts leaving the bag unloading stations. Note in the ducts the short metal spools connected to non-electrically-conducting flexible ducting. The metal spools are potential isolated conductors that could become charged.

Photo No. 4



Rectangular vessel is located on elevation below bag unloading station and is the small accumulation vessel. The inlet duct is made of metal and is wrapped with a cover to stop powder leaks.

Photo No. 5



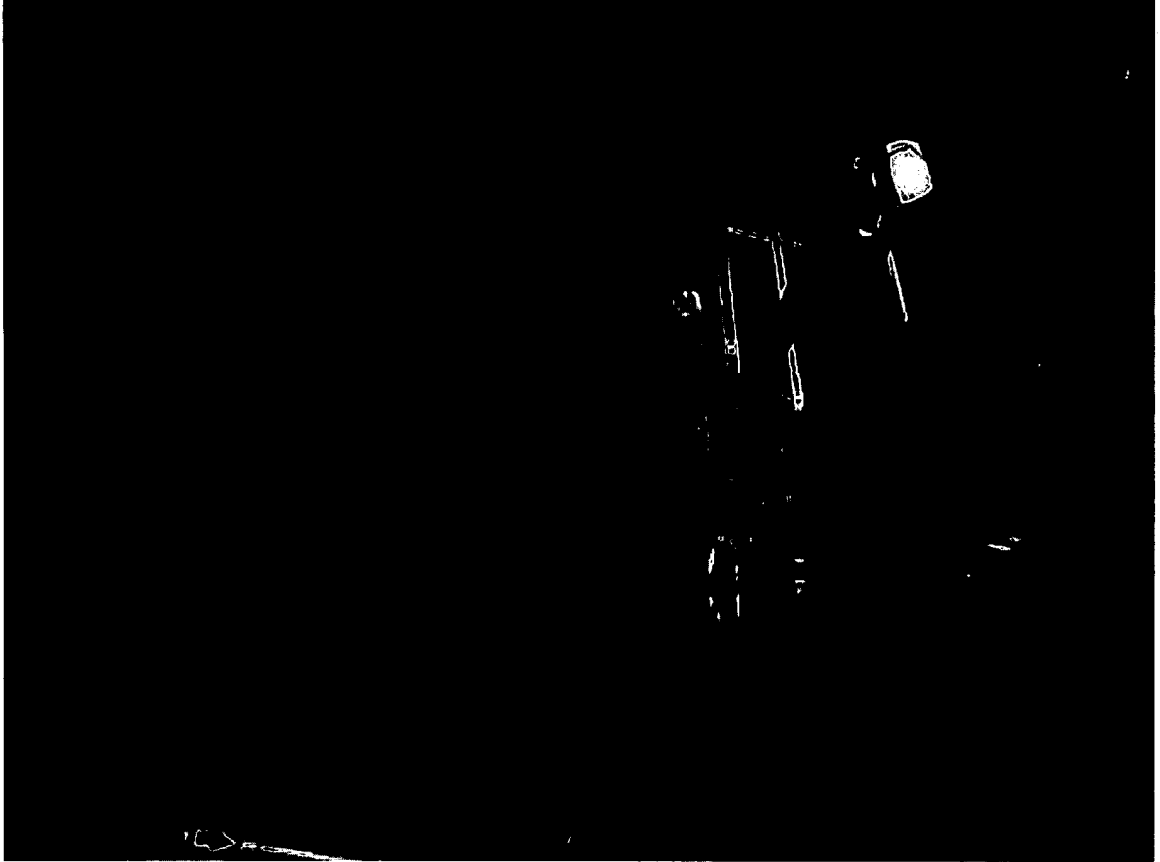
Small screw conveyer that potentially is used to feed Barricade™ 65 MC powder in to the mixing screw conveyer below. Powder to supply the small screw conveyer comes from the small accumulation vessel. There is a moving device inside the vessel that feed the screw conveyer.

Photo No. 6



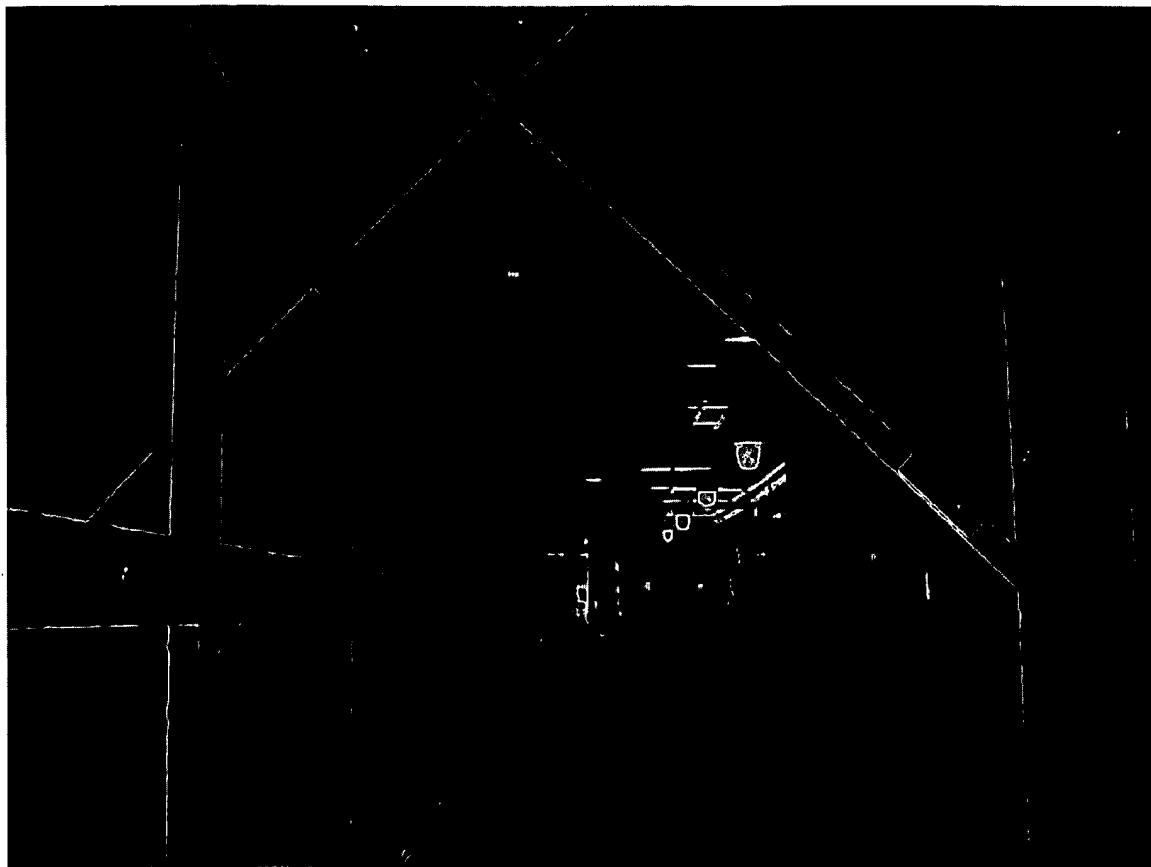
Mixing screw conveyer downstream of introduction point for Barricade™ 65 MC powder. The diameter of the screw from one end of a flight to the other is about nine inches.

Photo No. 7



View of bottom portion (dusty-air plenum) of dust collector.

Photo No. 8



Bottom of dust collector that shows location where collected dust is contained when bag-cleaning apparatus shakes dust off the surface of filter bags.

Information Sources

- “Avoiding Static Ignition Hazards in Chemical Operations”; by Laurence G. Britton; Center for Chemical Process Safety of the American Institute of Chemical Engineers; New York (1999).

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3 Park Avenue  
New York, New York 10016-5901 USA

- National Fire Protection Association (NFPA)  
1. Batterymarch Park  
Quincy, MA 02269-9101 USA

- NFPA 654, “Standard for the Prevention of Fire and Dust Explosions from the Manufacture, Processing and Handling of Combustible Particulate Solids”, 2000 Edition.
  - NFPA 77, “Recommended Practice of Static Electricity”, 2000 Edition.
- “Static Electricity, Rules for Plant Safety”, Edition 1977; Edited by Norbert Jaeger; CIBA Specialty Chemicals, Inc., Additives Division.